Seasonal variations of magnesium atoms in the mesosphere-thermosphere

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[1] UV radiances from the Global Ozone Monitoring Experiment (GOME) spectrometer on the ERS-2 satellite are used to determine long-term dayside temporal variations of the total vertical column density below 795 km of the meteoric metal species Mg and Mg^+ in the upper atmosphere. The GOME instrument has the ability to observe the ground state transition lines of Mg I at 285.2 nm and resolve the Mg II at 280 nm. A retrieval algorithm has been developed to determine column densities and applied to the years 1996–1997. Results show the middle latitude dayside Mg^+ peaks in total vertical content during the summer, while neutral Mg demonstrates a much more subtle maximum in summer. Dayside trends are opposite previous midlatitude nighttime lidar observations, with the exception of calcium. The Mg^+/Mg ratio has a seasonal variation, reaching a maximum in the summer. The total content of Mg^+ is twice that of neutral Mg. **Citation:** Correira, J., A. C. Aikin, J. M. Grebowsky, W. D. Pesnell, and J. P. Burrows (2008), Seasonal variations of magnesium atoms in the mesosphere-thermosphere, *Geophys. Res. Lett.*, *35*, L06103, doi:10.1029/2007GL033047.

1. Introduction

[2] Every day the Earth is showered with an estimated 10^4 kilograms of interplanetary material. The dominant sources of these meteoroids are debris from asteroids and comets. The incoming material heats up and is vaporized in the mesosphere and lower thermosphere. This meteoric ablation is the dominant source of metal atoms in the Earth's upper atmosphere and leads to long-lived ionospheric layers. Determining the atmospheric metal content provides a constraint on the estimate of the influx of extraplanetary dust to the Earth, its temporal variablity and provides a laboratory for studying metal chemistry in the upper atmosphere. Investigations into atmospheric metals have been conducted using ground-based airglow and lidar measurements, and measurements from sounding rockets, and satellites. Each of these techniques have unique capabilities.

[3] Ion mass spectrometers carried on sounding rockets and satellites have been useful in identifying all of the metal species associated with meteoric ablation [e.g., *Johnson and Meadows*, 1955; *Istomin and Pokhunkov*, 1963; *Narcisi and Bailey*, 1965; *Narcisi*, 1968; *Aikin and Goldberg*, 1973; *Grebowsky and Aikin*, 2002]. Although the rocket measurements provide precise altitude profiles of multiple metal species, they usually only measure ionized species. Also, sounding rockets can only be launched where suitable facilities exist and only give a snapshot of a particular location at a particular time.

[4] Light detection and ranging (lidar) overcomes the snapshot limitation of sounding rocket experiments by providing a long time baseline of observations. Although lidar provides high resolution altitude profiles of several neutral metal and ion species [see *Gerding et al.*, 2000; *Raizada and Tepley*, 2003] it has limitations as well. Lidar used for studying atmospheric metal species is typically limited to a few particular locations, like sounding rockets. Further, ground-based lidar experiments are commonly equipped to observe only one or two species, and cannot measure Mg and Mg^+ which are major deposition species. Most importantly, the majority of lidar observations have been limited to nighttime in order to take advantage of reduced background noise in the absence of atmospheric illumination by the sun.

[5] A more continuous and global method of observing metal atoms in the upper atmosphere is via remote observations from satellites. Early satellite-based ultraviolet spectrometers utilizing a limb scanning geometry have concentrated on the detection of Mg^+ in the thermosphere [*Gérard and Monfils*, 1974, 1978; *Mende et al.*, 1985], and more recently Fe^+ [*Dymond et al.*, 2003]. These studies however utilized only short snapshots of the ion distribution. The Solar Backscatter Ultraviolet/Total Ozone Mapping Spectrometer (SBUV/TOMS) aboard Nimbus 7 was the first instrument used to study the long-term seasonal and solar cycle variations of total vertical content of Mg^+. The Nimbus Mg^+ measurements were taken one day per month for about seven years [*Joiner and Aikin*, 1996] and included some neutral Mg measurments. The GLO-1 experiment flown aboard the space shuttle provided the first thermospheric altitude profiles of multiple metal species, including simultaneous observations of Mg and Mg^+ [*Gardner et al.*, 1995, 1999].

[6] A satellite instrument with the capability of adding new information on the metal atom distributions in the atmosphere is the Global Ozone Monitoring Experiment (GOME). GOME is a nadir viewing instrument on board the ERS-2 satellite, which was launched on 21 April 1995. The spacecraft is in a retrograde, sun-synchronous, 795 km high near-polar orbit with an equatorial crossing time of 10:30 AM local time and an orbital period of about 100 minutes. GOME data is available from 1996 until June 2003, when an on-board tape recorder failed. Earthshine spectra were recorded for wavelengths from 237 to 793 nm. The GOME instrument was designed to focus on the distributions of atmospheric constituents such as ozone,

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nitrogen dioxide, formaldehyde, bromine oxide, and water vapor but its spectral range includes lines of several metal atom species and their ions.

[7] GOME has several important advantages that add to and complement the other metal detection methods described above. It has extensive geospatial coverage, providing daytime pole-to-pole coverage every three days. It also measures the solar irradiance every 14 orbits, roughly once per day. This is a marked improvement over other resonant scattering studies that used a static reference solar spectrum. The GOME daily solar flux measurements allow variations in the solar irradiance to be taken into account. The GOME dataset provides a long baseline (1996–2003) and has good temporal resolution (1.5 or 12 seconds depending on the scanning mode) between consecutive measurements. It is useful for studying both short-term effects such as meteor showers, which could have characteristic variations of a few hours, and long-term phenomena such as solar cycle effects.

2.   Data Analysis

[8] The primary data product from the GOME instrument is the radiance or the number of photons per cm^2 per second per nanometer per steradian scattered in the zenith direction from atmospheric species. The metal vertical column densities are derived from photon counts using the airglow equation

$$4\pi J_m = g \int n(z)dz \qquad (1)$$

where J_m is the radiance integrated over a metal spectral line, $\int N dz$ is the sought after vertical column density, and g is the column photon emission rate, the 'g-factor', which is given by *Paxton and Anderson* [1992]

$$g = \frac{\pi e^2}{mc^2}\lambda^2 f\ \pi F(\lambda_0)P(\theta) \qquad (2)$$

with $\pi F(\lambda_0)$ the solar irradiance at the transition wavelength in units of photons per cm^2 per second per nanometer and f is the transition oscillator strength. We have included the anisotropic scattering phase function $P(\theta)$ [see *Chandrasekhar*, 1960, p. 50], where θ is the angle between the incident solar photon and the scattered photon. The symbols λ, e, m, and c represent wavelength, electron charge, electron mass and the speed of light, respectively.

[9] To derive the vertical metal column densities we must first calculate the background radiance within individual metal lines in order to determine how many photons would be counted in the absence of metal atoms in the atmosphere. This number is then subtracted from the observed photon fluxes to get the radiance due to resonant emission from the corresponding metal atoms. This procedure is simplified by the fact that attenuation of the incident solar flux in the wavelength region of interest is minimal above 80 km where the atomic metals prevail.

[10] The background radiance to solar irradiance ratio (basically the albedo) is a slowly varying function of wavelength, with its shape dominated by Rayleigh scattering and O_3 absorption. Peaks appear in this ratio, indicating wavelengths where photons are added to the radiance by resonant scatter of sunlight from metal species. In the region around the metal spectral line resonance peaks a spline is fit to the 'continuum' in this radiance to irradiance ratio. The spline is what the radiance to irradiance ratio would look like without resonant scatter from metal species. The spline is then multiplied by the solar irradiance to calculate what the radiance would look like without resonant scatter from metal species. Then the difference between the calculated metalless radiance and the GOME observed radiance are photons due to resonant scatter from metals, J_m, and equation (1) is solved for the vertical metal column densities. The Ring effect (Rotational Raman scattering) was not included in this analysis since it is a minor effect(<2% filling in of the solar Fraunhofer lines [see *Joiner and Aikin*, 1996]).

3.   Selection of Magnesium Measurements

[11] For this paper GOME Mg and Mg^+ data from the years 1996 and 1997 were analyzed, resulting in nearly 2 million column densities for each species. Data from the early phase of the mission in 1996–1997 provided an opportunity to analyze GOME data without the complication of correcting for instrument degradation. Atomic data used to calculate g-factors were taken from the National Institute of Standards and Technology Atomic Spectroscopy Database, available online at http://physics.nist.gov/asd3. Assuming a typical uncertainty of 3% for the radiance and irradiance [*Bednarz*, 1995], as well as for the oscillator strengths, the uncertainty of a single derived column density is estimated to be at least 6%, and is likely to be closer to 10% when taking into account errors due to the numerical fitting of spectral lines. For the present study the region of interest was restricted to ±40° latitude to avoid the complexities of high latitude oblique scattering and to minimize the local time variation. Focusing on the delineation of latitudinal seasonal variations of the metal column densities the data were broken down into 10° latitude bands. Within each 10° bin all observations were ordered chronologically and then a 500 point median smooth was applied (representing about 4 hours) in order to give a sense of overall trends. Each 10° latitude band contains approximately 125,000 data points. Figure 1 presents the smoothed Mg and Mg^+ column densities versus time. Figure 1 is broken down into four 10° latitude bands, beginning with a mid-northern latitude bin at the top, followed by low-northern latitude, low-southern latitude, and mid-southern latitude bin.

4.   Discussion

[12] As can be seen in all four panels of Figure 1 there are seasonal and latitudinal variations in both the Mg and Mg^+ column densities. The seasonal dependence is more pronounced away from the equator. The midlatitude ionized magnesium contents reach a maximum in the summer months and decrease to a minimum in the winter months. The neutral species has a much smaller seasonal dependence, with a nearly constant value in the northern hemisphere and slight summertime increase in the southern hemisphere. This hemispherical asymmetry in the seasonal behavior of the neutral is possibly tied to differences in
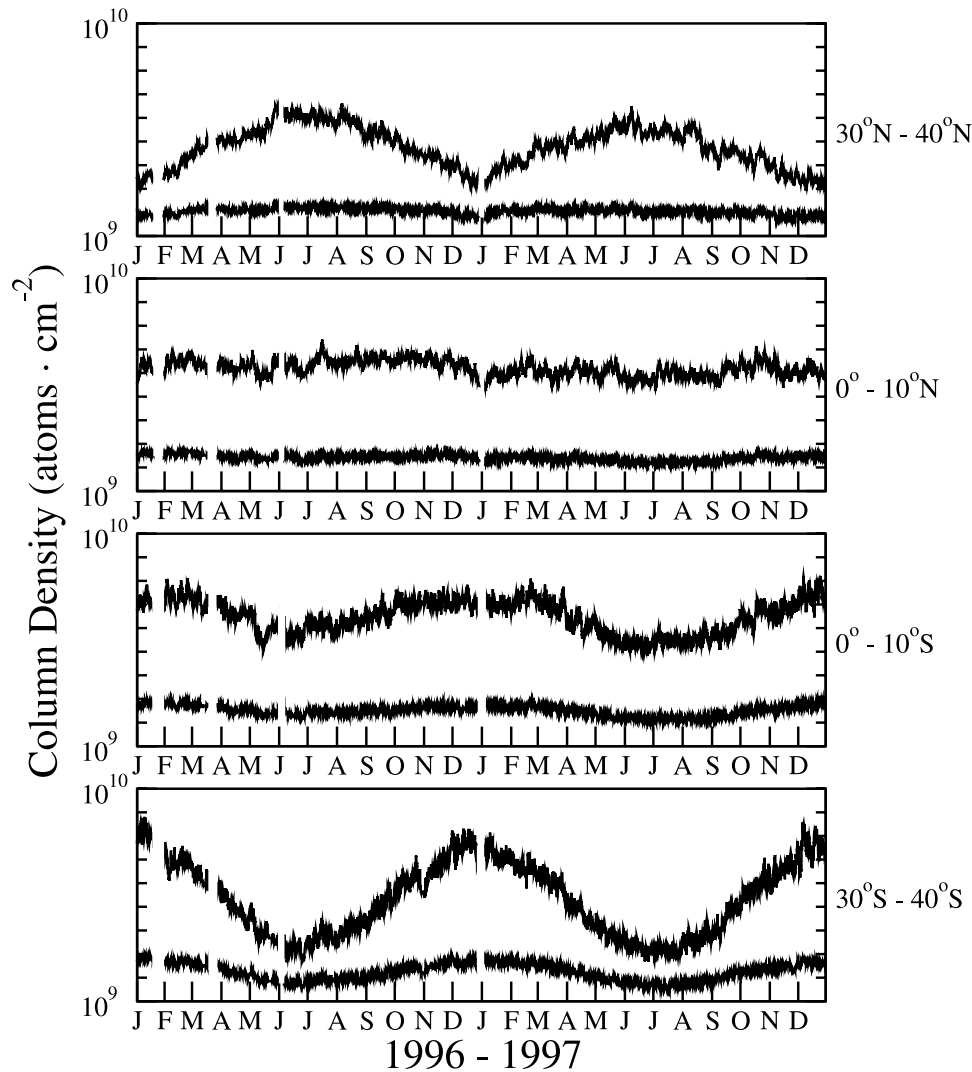
Figure 1. Vertical column densities for Mg (lower curve) and Mg$^+$ (upper curve). A 500 point median window was run over the raw data. The plots cover 30°N−40°N, 0°−10°N, 10°S−0°, and 30°S−40°S latitude from top to bottom.

seasonal temperature changes of northern and southern mesospheric temperatures (see, e.g., MSIS-90 model) [*Hedin*, 1991]. The individual southern hemisphere values shows more variability due to increased instrumental noise due to the Southern Atlantic Anomaly.

[13] Seasonal variations of meteoric metal atoms have been reported previously, commonly with a maximum in the winter and a summer minimum. Lithium [*Jegou et al.*, 1980] and sodium [*Plane et al.*, 1999] have a nighttime winter maximum, similar to the seasonal trends seen in the daytime by *Fan et al.* [2007] and *Gumbel et al.* [2007] using a satellite based spectrometer to derive the vertical column densities of sodium from limb scans. Potassium [*Eska et al.*, 1998; *Friedman et al.*, 2002] was found to have a different nighttime semiannual variation with a summer maximum. Lidar observations of calcium also found annual and semi-annual variations, with maxima in the summer and late autumn to early winter period [*Gerding et al.*, 2000]. Calcium, the only specie whose ionized form has been probed by lidar, has a column abundance of Ca$^+$ that is greatest in the summer [*Gerding et al.*, 2000].

[14] Magnesium has been commonly assumed to have a similar chemistry to that of iron, with some studies even using the same ion reaction rates [e.g., *McNeil et al.*, 2001]. Nighttime lidar observations of iron at mid-northern latitudes by *Kane and Gardner* [1993] found a seasonal variation with a winter maximum. This finding was supported by chemical modeling of the iron distributions [*Helmer et al.*, 1998]. A low latitude nighttime lidar study of iron by *Raizada and Tepley* [2003] reported a three month lag in neutral iron column densities when compared with the *McNeil et al.* [2001] study. Our GOME results show that daytime magnesium does not have the wintertime maximum expected given its assumed similarities to iron. Using NIMBUS satellite UV observations [*Joiner and Aikin*, 1996] found an annual variation in the Mg$^+$ with a summer maximum, in agreement with our results. A summertime increase in Mg$^+$ is perhaps not surprising based on nighttime lidar Ca$^+$ studies showing a summer maximum [*Gerding et al.*, 2000]. Magnesium and calcium have the same outer shell electron configurations so it is reasonable
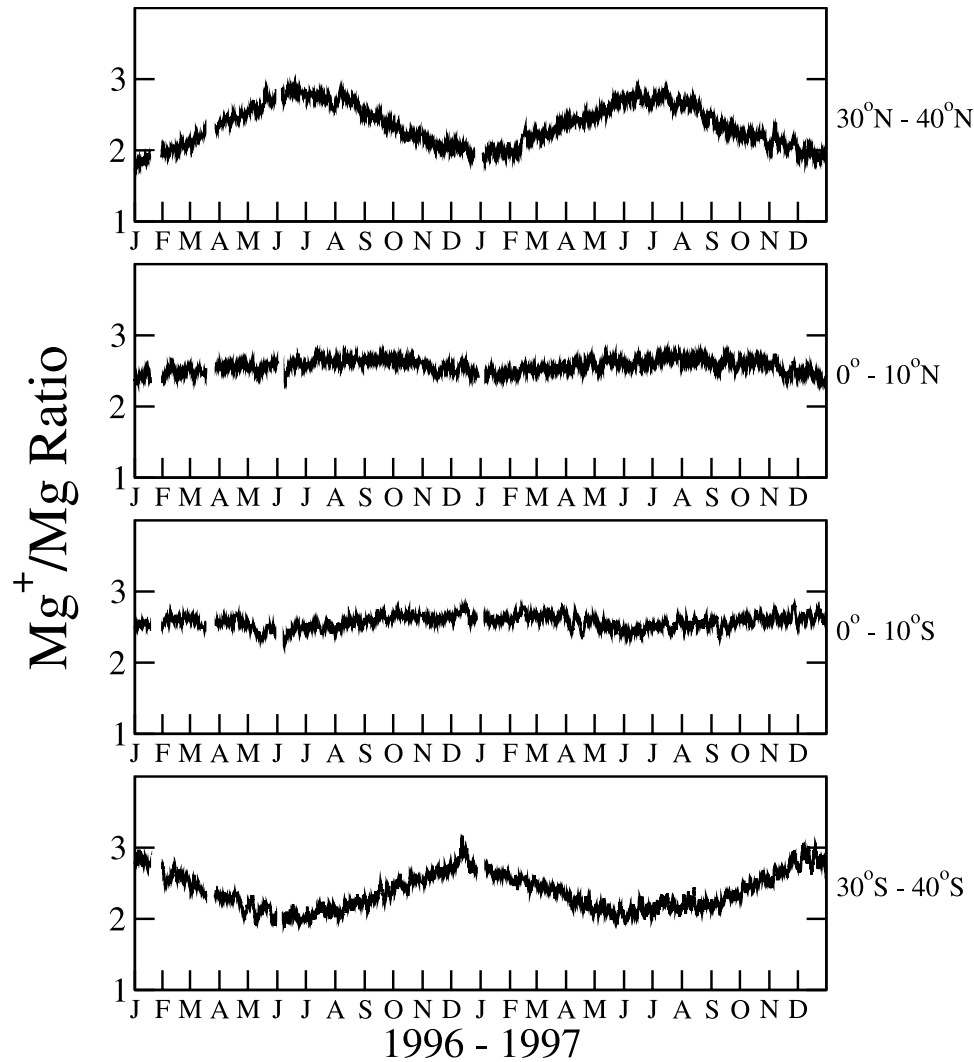
Figure 2. Ratio of singly ionized magnesium to neutral magnesium. The four latitude bands coincide with the latitude bands of Figure 1.

to expect that their ions would undergo similar chemical reactions and therefore have similar seasonal variations.

[15] The GOME Mg^+/Mg ratio (Figure 2) also has a seasonal dependence with a summer maximum at the middle latitudes. This can be understood by considering the processes which form Mg^+. The relevant reactions are described by *Pesnell and Grebowsky* [2000], a Mars study, replacing the Martian buffer CO_2 by the terrestrial third body N_2. Assuming photochemcial equilibrium the concentration of Mg^+ is directly proportional to the rate of photoionization of Mg. Mg^+ is also formed by charge exchange of Mg with lower ionospheric ions, which increase in the summer months [*Bilitza*, 2001]. It is also interesting to note that the Ca^+/Ca ratio of $\sim$2 from *Gerding et al.* [2000] closely matches our Mg^+/Mg ratio of approximately 2.5.

[16] As noted above, excepting Ca, all other neutral metallic metals have demonstrated a middle latitude maximum column density in the winter months and it has been assumed that magnesium would demonstrate a similar behavior. Modeling of the magnesium chemistry has also predicted a winter maximum [*Fritzenwallner and Kopp*, 1998]. However the previous studies concentrated on night time behavior, in contrast with the GOME daytime observations under consideration here. Diurnal changes in the concentrations of key atmospheric constituents may provide an explanation for differences between the current GOME results and previous lidar studies. For neutral Mg the chief loss process is the reaction with ozone to form MgO which can react with atomic oxygen to return to Mg. There is a diurnal variation of these two important species with less O_3 and more O present during the day than at night. This implies that the production of MgO is slower and the conversion of MgO back into Mg is faster during the day. Thus one would expect to see less Mg at night when compared to the daytime.

[17] Another possible explanation for the lack of a neutral magnesium wintertime peak maybe be found in the temperature dependent chemistry of neutral magnesium. Due in part to its inaccessibility by ground-based lidar, the magnesium chemistry has not been study as extensively as the other meteoric metal species (*Rollason and Plane* [2001]

and *Plane and Helmer* [1995] are notable exceptions). Reaction rates for magnesium compounds are often derived from comparable reactions involving other meteoric metal species (e.g., sodium). During the daytime, a small portion of Mg is converted to Mg^+ by photoionization and ion-molecule reactions, while the primary loss process for Mg is conversion to molecules, predominately MgO. The molecule MgO reacts with O_2, CO_2, and H_2O in the lower mesosphere to form MgO_2, $MgCO_3$, and $Mg(OH)_2$. The rates of the reactions that form these compounds are inversely proportional to the temperature. During the mid-latitude summers the mesospause temperature decreases relative to winter, implying a faster conversion of MgO into $MgCO_3$ or $Mg(OH)_2$ in summer. In particular, the formation of $Mg(OH)_2$ from a three body reaction of MgO with water, which is already rather fast, increases quickly as the temperature falls (*Plane and Helmer* [1995] find the rate to be proportional to $T^{-3.7}$). Additionally, more H_2O is available above 80 km during summertime [*Garcia and Solomon*, 1985] for the MgO + H_2O + M reaction (where M is any third body). $Mg(OH)_2$ then reacts quickly with atomic hydrogen to produce MgOH, which then reacts with atomic hydrogen again to yield atomic Mg. It is possible that the rates of the reactions involving atomic hydrogen (which are proportional to temperature) are not as fast as estimated, and that the rates of forming magnesium compounds and recycling those compounds back to atomic Mg balance out. Further chemical modeling will be necessary to determine the sensitivity of the concentration of magnesium, in addition to laboratory determination of still uncertain reaction rates and their dependence on temperature.

5. Conclusion

[18] Two years of GOME data has been processed to yield total atmospheric content for the species Mg and Mg^+. This two year long data set allows the seasonal variations of the content of these species to be determined. There is a summer maximum in the content Mg^+ for northern and southern hemispheres. Neutral magnesium also demonstrates a much smaller increase during local summer time. There is far less seasonal change near the equator than at $30°-40°$ north and south latitudes. It is likely that differing temperature dependence of the chemical reactions creating and recycling magnesium compounds effectively cancel out, eliminating a previously expected increase in the magnesium concentrations during wintertime. This hypothesis needs to be investigated further through detailed modeling of the atmospheric chemistry of meteoric metals. The long time baseline of GOME data, covering 8 complete years from 1995–2002, provides an opportunity for further study of annual variations as well as solar cycle effects upon meteoric metal abundances.

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